Facile Preparation of Nitrogen-Doped Activated Carbon for Carbon Dioxide Adsorption

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ABSTRACT

Nitrogen-doped activated carbons with high surface areas obtained from resorcinol and formaldehyde resins were evaluated as CO₂ adsorbents in a simulated flue gas stream under anhydrous and humid conditions. These carbons were prepared using two approaches, namely ammonia treatment without nitric acid pre-oxidation and amination after pre-oxidation. The pre-oxidation of activated carbons considerably enhanced the nitrogen incorporation during the amination process. The amination temperature affects the content and type of nitrogen incorporated onto the carbon surface, as determined by X-ray photoelectron spectroscopy, which enhances the specific adsorbent-adsorbate interaction for CO₂ in humid conditions. The presence of H₂O in the feed gas significantly decreased CO₂ adsorption for a very low nitrogen content of virgin activated carbon. A sample prepared via the amination of pre-oxidized carbon at 700°C (NORF700) exhibited excellent tolerance to moisture and the highest CO₂ capacity of 2.10 mmol/g in a 7% CO₂/83% N₂/10% H₂O wet stream at 50°C and 130 kPa. The high performance of NORF700 was ascribed to its high surface area, adequate micropore volume, and high amounts of pyridinic-like and pyrrole-like nitrogen species. The results indicate that nitric acid pre-oxidation followed by ammonia treatment at 700°C is an appropriate process for preparing adsorbents for CO₂ separation in post-combustion applications.

Keywords: Activated carbon; Ammonia treatment; CO₂ adsorption.

INTRODUCTION

Due to global climate change, the increased concentrations of greenhouse gases have become a concern. Among greenhouse gases, carbon dioxide (CO₂), released by the combustion of fuels and from certain industrial and resource extraction processes, makes the largest contribution to anthropogenic climate change (Plaza et al., 2008). To reduce CO₂ emissions at industrial sites, the development of materials and technologies for CO₂ capture and sequestration has attracted the largest contribution to anthropogenic climate change (Plaza et al., 2008). For the post-combustion process, conventional monoethanolamine (MEA)-based solvent and wet scrubbing systems have been widely used for over 60 years, but they are energy intensive due to the required large amount of water (Arenillas et al., 2005). The drawbacks of capturing CO₂ using the MEA process are high corrosion potential, large MEA losses due to vaporization and degradation, and high energy consumption. To regenerate the solvent, a typical energy penalty incurred for the MEA capture process is an estimated 14% of the net power output of the plant (Rao and Rubin, 2002). Numerous alternatives, such as cryogenic separation, membrane separation, micro algal bio-fixation, and adsorption, are available for sequestering CO₂ from flue gases from the combustion of fossil fuels (Thiruvenkatachari et al., 2009). Adsorption is attractive due to its low energy requirement, low cost, and good cycle performance. Recently, a number of porous adsorbents, such as metal-organic frameworks (MOFs), porous silica, zeolite, and activated carbons (ACs), have been developed for CO₂ capture. For MOFs, the major problems are their powder form and poor chemical and thermal stability, which are major obstacles to their effective use in realistic conditions. Amine-surface-modified or amine-impregnated porous silica (e.g., MCM-41, MCM-48, and SBA-15) materials lack stability over many cycles (Chang et al., 2003; Hiyoshi et al., 2005; Bhagiyalakshmi et al., 2010). Although zeolitic imidazolate frameworks exhibit a high affinity for CO₂ molecules at low pressures and a higher selectivity for CO₂ from other relevant fuel gases, their use in CO₂ capture
often suffers from structural instability and inefficient CO₂ selectivity in the presence of water, limiting their widespread use (Wang et al., 2008). In contrast to the poor adsorption capacity of zeolites in the presence of moisture, carbon materials are relatively insensitive to moisture and are suitable candidates for CO₂ capture due to their pore structure and surface chemistry properties. The basic surface of carbon materials ensures a good adsorption for CO₂ since CO₂ is a weak Lewis acid (electron acceptor) that can interact with electron donors, such as nitrogen surface groups. Recently, basic nitrogen groups have been incorporated onto AC frameworks for enhancing CO₂ adsorption (Gray et al., 2004; Plaza et al., 2009; Plaza et al., 2011). Nitrogen-containing functionalities can be introduced in the carbon matrix via a reaction with nitrogen-containing reagents (i.e., NH₃, urea, and amines) or the preparation of a carbon from a nitrogen-containing precursor (i.e., carbazole, melamine, acridine) (Stoeckli et al., 1996; Lopez et al., 2000; Carrott et al., 2001; Plaza et al., 2011; Plaza et al., 2009). Plaza et al. (2010) modified AC with gaseous ammonia at temperatures from 400 to 900°C and found that the optimum temperature was 800°C, at which CO₂ adsorption capacity and nitrogen incorporation reached their maximum values. For gaseous ammonia to be strongly adsorbed at ambient conditions, the use of an adsorbent with an acidic surface is required. AC does not fully meet the above requirement since its surface acidity is insufficient. However, the surface chemistry of AC is quite easy to modify and can lead to the formation of strong interactions between gaseous ammonia and AC. Due to the small size (3 Å) and basic chemistry of ammonia gas, effective adsorption of NH₃ requires an acidic adsorbate surface and specific interactions between NH₃ molecules and the adsorbate surface, including hydrogen bonding, acid-base reactions, and complexation. AC can be given an acidic surface by heating it in an air flow (Le Leuch et al., 2007) or oxidizing it using an oxidizing agent (Tamon et al., 1996). Using an oxidizing agent such as nitric acid is a convenient way to form acidic groups on AC, since nitric acid has been shown to be a very effective oxidizing agent for the introduction of a significant number of oxygenated acidic functionalities in the form of carboxylic and phenolic hydroxyl groups onto the carbon surface (Puri, 1970).

Most post-combustion power plant flue gas includes 68–75% N₂, 10–15% CO₂, 5–10% H₂O, 2–5% O₂, and trace amounts of NO and SO₂. The overwhelming majority of published research deals with dry feed gas, even though real flue gas contains a high level of saturated water vapor. The present study thus investigates the influence of N doping on the textural properties and surface basicity strength of AC applied to CO₂ adsorption from a simulated moist flue gas. A comprehensive study of the kinetic CO₂ adsorption under dry and wet gas streams was conducted using a wide range of carbon materials, including virgin carbon, carbon with NH₃ gas heat treatment without nitric acid pre-oxidation, and carbon with nitric acid pre-oxidation and heat treatment with NH₃ gas at various temperatures.  

### Experimental Procedure

#### Preparation of Resorcinol-Formaldehyde AC

In a typical synthesis of aqueous organic gel, 5.71 g of resorcinol (R) and 0.14 g of sodium hydroxide were dissolved in a solvent mixture of ethanol (38.00 g) and deionized water (36.00 g) with magnetic stirring at 25°C. After dissolution, 2.01 g of 37 wt.% formaldehyde (F) was added and the mixture was stirred until a homogeneous solution was obtained. After curing (3 days at 50°C under vacuum), the dried polymer was heated at 400°C (5 h) under an N₂ atmosphere, and thus was carbonized into char. The obtained char was ground in an agate mortar and mixed with aqueous KOH solution (char:KOH concentration of 1:4 g/g) and distilled water (10 mL water per 2 g KOH). The mixture was kept at 85°C for 4 h under stirring and then dried at 110°C for 8 h. The activated char was carbonized at 800°C under N₂ flow at a flow rate of 100 mL/min and a ramping rate of 5 °C/min. Finally, the carbonized carbon was cooled and washed in 0.1 M HCl solution to remove residual KOH, and further dried with distilled water several times until the solution pH reached 7. The product (denoted as RFAC) was collected by filtration and dried in an oven at 110°C for 12 h.

#### Surface Modification Using NH₃ Gas

For preparing oxidized AC, 1.00 g of the dried resorcinol-formaldehyde AC was oxidized with 6 N HNO₃ at 80°C for 8 h (ratio of 1 g carbon/10 cm³ HNO₃ solution). The oxidized samples were then thoroughly washed with water to remove excess acid and the water-soluble products of oxidation, and finally dried at 110°C for 6 h. The acid treatment resulted in the formation of oxygenated AC.

For surface modification with NH₃ gas (amination) with oxidation, the obtained oxidized AC was loaded into the furnace, heated in an NH₃/N₂ mixture (80/20% v/v) with a heating rate of 10°C/min from room temperature until the defined amination temperature, and then held for 2 h. After heat treatment, the furnace was cooled to 100°C, and the NH₃/N₂ mixture flow was switched to N₂. The furnace was then allowed to cool down to room temperature. The NH₃/N₂ mixture and N₂ flow rates were both set at 50 cm³/min. The carbons obtained with pre-oxidation, denoted by the letter O, followed by NH₃ gas heat-treatment at 600, 700, and 800°C were designated NORF600, NORF700, and NORF800, respectively. To study the effect of pre-oxidation on the properties of the samples, an AC (denoted as NRF700) was prepared via amination treatment at 700°C without nitric acid pre-oxidation.

#### Characterizations of Samples

Ultimate analysis was carried out using an elemental analyzer (Elementar, Vario EL) to determine the chemical composition of the carbon samples. The carbon, hydrogen, and nitrogen content of the samples were determined directly, and the oxygen content was obtained by subtracting total content from C, H, and N. The chemical states of the nitrogen element of the samples were determined at room temperature using X-ray photoelectron spectroscopy (XPS) (Kratos Axis, Ultra DLD) with an Al Kα source. For calibration, the C 1s electron binding energy was set to 285.0 eV.
eV and the distributions of N-containing functionalities were quantified after fitting the XPS N Is peaks into Gaussian- Lorentzian component profiles. The FTIR spectra of the samples were measured using a FTIR spectrometer (PerkinElmer, FTIR-2000). 0.1 g of AC was encapsulated in 1 g of KBr as the testing pellet. Moreover, a diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS, was adopted to observe directly the interaction between activated carbons and adsorbent (carbon dioxide), to study in-situ FT-IR spectra of activated carbon after exposure to various environments. In situ DRIFTS measurements were performed using a PerkinElmer FTIR spectrometer (spectrum GX) and a diffuse reflectance accessory (Harrick Scientific, DRP-PE9) with a reaction cell (Harrick Scientific, HVC-DRP-3). The sample was placed in an airtight cell, equipped with a ZnSe window, had connections for inlet and outlet gas flows controlled by mass-flow controllers and the cell temperature was maintained by a heating element and a thermocouple, providing the feedback to a temperature controller to maintain the temperature constant. A total of 128 scans were recorded per spectrum over the range 4000–800 cm⁻¹ at a resolution of 4 cm⁻¹. To improve the reflectivity of the samples, the samples were diluted with KBr and the ratio of KBr to sample was 20/1. A spectrum of KBr recorded in N₂ was set as background. The textural characterization of the samples was determined from the N₂ adsorption/desorption isotherms conducted in a volumetric apparatus (Micromeritics, ASAP 2020). The AC was degassed at 473°C in a vacuum for a period of at least 4 h prior to measurements. The nitrogen adsorption/desorption isotherms were measured over a relative pressure (P/P₀) range of approximately 10⁻³ to 0.995. The Brunauer-Emmett-Teller (BET) surface area of the AC (S_BET) was calculated from N₂ adsorption isotherms with the BET equation using adsorption data in the P/P₀ range of 0.06 to 0.2. The total pore volumes (V_pore) were estimated from the adsorbed N₂ amount at P/P₀ = 0.973. The pore size distribution (PSD) in the micro- and mesopore regions was determined by applying the density functional theory (DFT) method based on nitrogen adsorption data.

**Dynamic Adsorption Capacity of Carbon Dioxide**

CO₂ breakthrough experiments were performed in a stainless tubular column (i.d.: 20 mm; length: 120 mm) equipped with a porous plate located 30 mm from the base of the column, which was placed vertically inside a tubular furnace. 0.20 g of AC powder was used to get the required breakthrough capacity. In a typical experiment, adsorbents were regenerated prior to each breakthrough test by heating the stainless tubular column up to 150°C for 1 h while purging with 100 NmL/min of N₂. The stainless tubular column was then cooled to 50°C. After pretreatment, the desired flow of N₂ and the selected CO₂ flow were added to the mixing tank as an N₂/CO₂ mixture (83/17 % v/v) with a total gas flow rate of 100 NmL/min. Since the moisture was contained in a coal-fired combustion stream, the adsorbent performance measurements were conducted under moist feed mode. To create moist conditions, saturated water vapor was obtained by passing N₂/CO₂ gas through a small-scale water tank in a constant temperature water bath at 50°C to produce an N₂/CO₂/H₂O mixture (83/10/7 % v/v) with a total gas flow rate of 100 NmL/min. The carbon dioxide concentration of the outlet gas stream was measured by a BABUC BSO103 CO₂ continuous monitoring system interfaced with a computer data acquisition program. The adsorption capacities of each carbon were calculated by integrating the area above the breakthrough curves, and from the total flow rate, CO₂ concentration in the inlet gas, flow rate, breakthrough time, and mass of carbon. The dynamic adsorption capacity is calculated from the breakthrough curve as:

$$Q_{dy} = \frac{F_{Cin} \cdot S}{M}$$

where $Q_{dy}$ is the dynamic adsorption capacity (mg/g-adsorbent), $F$ is the total flow rate (mL/min), $C_{in}$ is the concentration of CO₂ entering the column (vol.%), $M$ is the mass of adsorbent loaded in the column (g), and $t_d$ is the stoichiometric time corresponding to CO₂ stoichiometric adsorption capacity (min). The stoichiometric adsorption capacity is the area between the breakthrough curve and a line at $C_{out}/C_{in} = 1.0$.

**RESULTS AND DISCUSSION**

**FTIR Spectra of Initial and Modified Samples**

To investigate the effect of pre-oxidation on the functional groups present on the surface of the samples, a carbon denoted as ORFAC was prepared by the oxidation of nitric acid. By measuring the FTIR spectra of the samples before and after modification, surface functional groups formed or consumed during treatment can be obtained. Fig. 1 shows the results of FTIR measurements for initial carbon and surface-modified samples. In Fig. 1(a), there is a peak around 1020–1030 cm⁻¹ for initial carbon (RFAC), which can be attributed to the C-O stretching of ethers. After pre-oxidation, peaks at 1729 and 1595 cm⁻¹ and a broad band from 900 to 1300 cm⁻¹ appear for ORFAC. The peaks at 1729 and 1595 cm⁻¹ are assigned to C=O group in the micro- and mesopore regions was determined by applying the density functional theory (DFT) method based on nitrogen adsorption data.
their intensities, indicating small differences in the surface chemistry. A band at around 1565 cm\(^{-1}\) can be ascribed to the N-H group for all NORF samples. A comparison of spectra for samples with amination without preliminary oxidation (NRF700) and those with amination and oxidation (NORF series) shows obvious changes in the range of 3376 and 3294 cm\(^{-1}\). The broad band in the 3376 to 3294 cm\(^{-1}\) region is associated with overlapping bands of O-H and N-H stretching vibrations, which might be related to the formation of hydrogen bonds between the adsorbed NH\(_3\) molecules and oxygen surface groups (Gómez-Serrano et al., 1994).

**Textural Properties of Initial and Modified ACs**

The N\(_2\) adsorption-desorption isotherms for various AC samples are shown in Fig. 2. It is clear that the shapes of modified ACs are different from that of the initial AC. The major update of initial AC (RFAC) occurred at a relative pressure of around 0.2, and remained almost constant at higher relative pressures, indicating that RFAC was mainly a microporous material. For NORF800, the isotherm became a combination of I and II, indicating the presence of a number of mesopores. To determine the porosity development of the AC samples before and after modification, the pore size distributions, calculated using the DFT model, are shown in Fig. 3. As can be seen, all types of AC possessed micropores and mesopores. It can be observed that pre-oxidation followed by the ammonia process leads to the development of pores in the carbon and causes an increase in the numbers of ultramicropores (< 0.7 nm), supermicropores (0.7–2 nm), and mesopores (2–50 nm), especially for NORF800. The surface area, micropore area, pore volume, and average pore size of ACs are summarized in Table 1. The results show that after amination, the total surface area, micropore area, and pore volume of NRF700, NORF600, and NORF800 decreased compared to those of RFAC. NORF800 has the smallest \(S_{BET}\) value, micropore area, and pore volume of the NORF series, indicating that an amination temperature of 800°C is detrimental to textural development.

A comparison of the textural properties (see Table 1) between NRF700 (amination without preliminary oxidation) and NORF700 (pre-oxidation followed by amination) shows that pre-oxidation promotes the increases of the surface area, micropore volume, and pore volume of the sample. When the oxidized carbons were treated with ammonia at high temperatures, the NH\(_3\), NH, and atomic hydrogen radicals created during ammonia decomposition may have attached to the surface oxides and released CO\(_2\) or CO (Pevida et al., 2008), resulting in increased surface area and pore volume for NORF700. The mesopore volume for the modified ACs increased, especially for NORF700 and NORF800. This increase may be associated with the enlargement of micropores, indicating that mesopores and macropores increased with increasing temperature.

**Nitrogen Content and Type of Nitrogen-containing Functionalities**

Since CO\(_2\) is an acidic gas, alkaline surface functional groups like nitrogen species on the AC surface improve the chemisorption of CO\(_2\) from flue gas (Hsiao et al., 2011). Elemental analysis (EA) and high-resolution XPS analyses were used to determine the nitrogen content and type of nitrogen-containing functionalities in the samples, respectively. The results obtained from EA presented in Table 2 show an increase of the nitrogen content after surface modification with amination, particularly for NORF carbons. For instance, the nitrogen content increased from less than 0.2 wt.% for initial carbon (RFAC) to 1.1 wt.% for NRF700 and 7.2 wt.% for NORF700. Moreover, the incorporation of nitrogen is significant for NORF700, which had 6 times more nitrogen than did NRF700, which was treated at the same temperature without pre-oxidation. The differences in nitrogen content between the NORF700 and NRF700 samples indicates that the presence of oxygen functionalities on the carbon surface before amination plays an important role in determining the degree of nitrogen incorporation into the surface, and that the pre-oxidation of carbons considerably enhances nitrogen incorporation during...
 ammonia treatment (Table 2). It has been reported that the free radicals (such as NH₂, NH, and atomic hydrogen) created during ammonia decomposition may attach to the surface oxides or active sites present on the carbon surface to form nitrogen-containing functional groups (Stöhr et al., 1991; Bota and Abotsi, 1994; Vinke et al., 1994). Temperature also influences the amount of nitrogen incorporated into the carbon surface. For temperatures higher than 700°C, less nitrogen was incorporated into the modified carbon in this study.

High-resolution N 1s spectra of various samples are shown in Fig. 4. Each of the XPS spectra was obtained using four Gaussian curves based on the four species of nitrogen reported in the literature. These nitrogen species could be assigned to pyridinic (N-6, 398.5 eV), pyrrolic/pyridone (N-5, 400.2 eV), quaternary (N-Q, 401.2 eV), and pyridine-
Table 2. Carbon, hydrogen, oxygen, and nitrogen content of samples obtained from elemental analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate analysis (wt.%, dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>RFAC</td>
<td>81.80</td>
</tr>
<tr>
<td>NRF700</td>
<td>70.28</td>
</tr>
<tr>
<td>NORF600</td>
<td>50.24</td>
</tr>
<tr>
<td>NORF700</td>
<td>76.56</td>
</tr>
<tr>
<td>NORF800</td>
<td>53.48</td>
</tr>
</tbody>
</table>

* Calculated by difference.

Fig. 4. High-resolution fitted XPS spectra of N 1s peak of (a) RFAC, (b) NORF600, (c) NORF700, and (d) NORF800.

N-oxide (403.0 eV), respectively (Pinero et al., 2003). The amount of various N functionalities on the samples was obtained by integrating the four individual curves, as shown in Table 3. As can be seen, amination treatment leads to an obvious change in the number and kind of nitrogen species in the samples. Amination increases the overall contribution of pyridinic (N-6) and pyrrolic/pyridone (N-5) for NORF600, NORF700, and NORF800. Taking into account that more nitrogen is incorporated for amination samples, the highest amount of nitrogen was obtained for NORF700. Moreover, more quaternary nitrogen, a very stable species, was found in NORF800 than in NORF600 and NORF700, indicating that pyridinic and pyrrolic functionalities transform into quaternary nitrogen at higher temperature.

Dynamic CO₂ Adsorption

Dynamic CO₂ adsorption and breakthrough in a 17% CO₂/83% N₂ stream under dry conditions and a 7% CO₂/83% N₂/10% H₂O stream under moist conditions are plotted as functions of time in Fig. 5 for various AC samples. As shown in Fig. 5(a), at the beginning of the anhydrous experiment, all the incoming CO₂ was adsorbed. After 1 min, the mass transfer zone reached the bed outlet and then CO₂ was detected in the effluent stream for RFAC, NRF700, NORF600, and NORF700. RFAC had the broadest breakthrough curve, whereas NRF700 and NORF800 had the steepest curves, indicating that intraparticle diffusion was the mass...
### Table 3. Results of curve fitting of the contribution of nitrogen species to N 1s peak of initial and modified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy (eV)</th>
<th>Total area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-6 (pyridinic)</td>
<td></td>
</tr>
<tr>
<td>RFAC</td>
<td>15.73</td>
<td>60.54</td>
</tr>
<tr>
<td>NORF600</td>
<td>412.70</td>
<td>1013.73</td>
</tr>
<tr>
<td>NORF700</td>
<td>360.63</td>
<td>1392.67</td>
</tr>
<tr>
<td>NORF800</td>
<td>338.10</td>
<td>1076.4</td>
</tr>
<tr>
<td></td>
<td>N-5 (pyrrolic/pyridone)</td>
<td></td>
</tr>
<tr>
<td>RFAC</td>
<td>24.43</td>
<td></td>
</tr>
<tr>
<td>NORF600</td>
<td>374.52</td>
<td></td>
</tr>
<tr>
<td>NORF700</td>
<td>588.37</td>
<td></td>
</tr>
<tr>
<td>NORF800</td>
<td>459.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N-Q (quaternary nitrogen)</td>
<td></td>
</tr>
<tr>
<td>RFAC</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>NORF600</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>NORF700</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>NORF800</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pyridine-N-oxide</td>
<td></td>
</tr>
<tr>
<td>RFAC</td>
<td>20.28</td>
<td></td>
</tr>
<tr>
<td>NORF600</td>
<td>226.41</td>
<td></td>
</tr>
<tr>
<td>NORF700</td>
<td>443.57</td>
<td></td>
</tr>
<tr>
<td>NORF800</td>
<td>1076.4</td>
<td></td>
</tr>
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</table>

**Fig. 5.** Comparison of breakthrough curves of CO₂ adsorption for various activated carbon samples for (a) dry stream and (b) wet stream (adsorption at 50°C and total gas flow rate of 100 NmL/min).

Transfer limiting mechanism. NRF700 and NORF800 exhibited high amounts of mesopores, which formed during the activation process; therefore, intraparticle mass transfer resistance was substantially reduced. From the breakthrough curve data, the dynamic adsorption capacities of obtained samples are given in Table 4. The adsorption performance of CO₂ follows the order: RFAC > NORF700 > NORF600 > NRF700 > NORF800. It is generally accepted that both textural properties and surface basicity strength influence the adsorption performance of CO₂. Therefore,

### Table 4. CO₂ breakthrough capacity of initial and modified samples under dry and moist conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry conditions (mmol/g)</th>
<th>Humid conditions (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFAC</td>
<td>1.80</td>
<td>1.61</td>
</tr>
<tr>
<td>NRF700</td>
<td>1.19</td>
<td>1.25</td>
</tr>
<tr>
<td>NORF600</td>
<td>1.38</td>
<td>1.81</td>
</tr>
<tr>
<td>NORF700</td>
<td>1.56</td>
<td>2.10</td>
</tr>
<tr>
<td>NORF800</td>
<td>1.10</td>
<td>1.49</td>
</tr>
</tbody>
</table>
adsorption performance was correlated to specific surface area, pore volume, pore size, and number of nitrogen functional groups of the samples. A plot of the amount of CO$_2$ adsorbed under dry conditions versus micropore volume (including ultramicropores and supermicropores) is given in Fig. 6. There is a linear relationship between the amount of CO$_2$ adsorbed and the micropore volume. Based on the results of EA and XPS, RFAC has the lowest nitrogen content, implying that the surface basicity of AC is not beneficial for CO$_2$ adsorption under anhydrous conditions.

Fig. 5(b) shows the results of the breakthrough experiments for the separation of CO$_2$ from a 7% CO$_2$/83% N$_2$/10% H$_2$O wet stream (100% relative humidity (RH)) using five samples. The saturation time of the adsorption bed became longer compared to that for the dry condition, except for RFAC. This indicates that water on the surface significantly increases the breakthrough time for modified samples. Moreover, pre-oxidation followed by amination, especially at 700°C, resulted in better adsorbents. For amination, pre-oxidation of the carbon dramatically increases the adsorption capacity. For instance, a 1.05 times enhancement of the adsorption capacity is for NRF700; those for NORF600, NRF700, and NORF800 are 1.31, 1.34, and 1.35, respectively, as indicated in Table 4. Under wet conditions, much worse performance was obtained, with the 0.89 time decrease for RFAC, virgin carbon. The existence of moisture may greatly influence the CO$_2$ capture performance of low-nitrogen-content RFAC due to the competition for adsorption between water and carbon dioxide on the surface of RFAC. It has been reported that moisture adversely affects CO$_2$ uptake in a variety of physical adsorbents, such as zeolites and carbonic (Hsiao et al., 2011). However, the highly humid flue gas, including 5–10% saturated water vapor, are treated in most of the post-combustion carbon captures projects (Ahn and Changha, 2004). Therefore, the development of new adsorbents for CO$_2$ removal from post-combustion flue gas should consider the tolerance to moisture. The reaction mechanisms between CO$_2$ and supported amine groups producing ammonium carbamate and ammonium bicarbonate in dry and humid streams, respectively, are (daSilva and Svendsen, 2007):

$$2(RNH_2) + CO_2 \leftrightarrow RNHCO_2^+ + 2H_2O \leftrightarrow (RNH_2^+)CO_3^{2-}$$

(2)

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNHCO_3^- + CO_2$$

(3)

Leal et al. (1995) found that one bidentate ammonium carbamate molecule converted into two monodentate ammonium bicarbonate molecules when water vapor was present in the gas feed, resulting in an obvious increase from 0.41 to 0.89 mmol/g using (3-aminopropyl)triethoxysilane/silica gel under a pure CO$_2$ flow with an RH of 100%. In the present study, the enhanced CO$_2$ adsorption for NORF600 and NORF700 in the humid stream may be attributed to the high nitrogen content. However, it should be pointed out that although NORF800 has a higher nitrogen content compared to that of NORF600, its CO$_2$ adsorption capacity is lower. These differences might be related to the types of nitrogen species on the AC surface. As shown in Table 3, both NORF600 and NORF700 have relatively high amounts of pyridinic-like nitrogen species (pyridine and pyridine-N-oxide) and pyrrole-like type nitrogen species compared to those of NORF800. In contrast, the carbon treated with pre-oxidation followed by ammonia treatment at the highest temperature (800°C), NORF800, had the highest amount of the most stable species (quaternary nitrogen), resulting in a lower CO$_2$ adsorption capacity than that of NORF600. Thus, the affinity between CO$_2$ and adsorbent depends not only on the amount of total nitrogen incorporated into the carbons but also on the type of nitrogen-containing functionalities introduced during the modification process. For comparison, the adsorption capacities of mesoporous silica and carbon materials obtained from the literature are given in Table 5. NORF700 has a higher CO$_2$ adsorption

![Fig. 6. Relationship between micropore volume and amount of CO$_2$ adsorbed on activated carbons under dry conditions.](image-url)
capacity than those of mesoporous silica and carbon evaluated under similar operating conditions (Na et al., 2001; Cinke et al., 2003; Huang et al., 2003; Hiyoshi et al., 2005; Drese et al., 2009).

**DRIFTS Study for NORF700**

DRIFTS studies have been successfully applied in studying the sorption kinetics of physisorbed and chemisorbed species on the NORF700 sorbent surface under dry and wet conditions. All measurements were carried out on a ca. 50-mg fresh sample previously pretreated in situ in flowing N2 conditions. All measurements were carried out on ca. 50-on the NORF700 sorbent surface under dry and wet conditions. It can be seen that the DRIFT spectra could be divided into three regions: 3800–2300 cm \(^{-1}\), 2300–1700 cm \(^{-1}\), and 1700–1200 cm \(^{-1}\). A comparison of Figs. 7(a) and 7(b) indicates that the introduction of H2O-vapor results in the increase of intensity of physisorbed CO2. Since the areas of the IR absorption peaks are proportional to molar adsorbed amounts, the physisorbed CO2 molecules in wet stream are much more abundant than those of dry stream. Moreover, a prominent sharp band of H–O–H bending at 1645 cm \(^{-1}\) and an intense and broad related to the H-bonded OH stretching vibration in the 3690–3700 cm \(^{-1}\) and 3250–3400 cm \(^{-1}\) were observed for NORF700 in wet condition. This was due to the increase in amount of H2O molecules from N2/CO2/H2O stream.

**CONCLUSION**

A series of nitrogen-doped AC samples was evaluated as potential adsorbents for separating CO2 from post-combustion flue gas under dry and wet conditions. Two
methods were employed to obtain nitrogen-doped AC samples, namely amination without nitric acid pre-oxidation and nitric acid pre-oxidation followed by amination at various temperatures. Preliminary oxidation significantly improves the nitrogen incorporation into the carbon surface during amination treatment. The increase of nitrogen content of the obtained samples was confirmed using FTIR, EA, and XPS. Amination temperature also influences the content and type of nitrogen incorporated onto the carbon surface. For temperature higher than 700°C, less nitrogen was incorporated into the pre-oxidized carbon. CO₂ breakthrough experiments performed under dry conditions demonstrated that the adsorption performance of CO₂ is closely related to the micropore volume of AC. The introduction of basic nitrogen surface groups, particularly through pre-oxidation followed by amination, significantly enhanced the adsorption ability of the carbon adsorbent towards CO₂ from a 7% CO₂/83% N₂/10% H₂O wet stream (100% RH). In contrast, the existence of moisture had a detrimental effect on CO₂ adsorption of very-low-nitrogen-content virgin AC due to the competition of adsorption between water and carbon dioxide on the surface. The NORF700 sample (pre-oxidation and amination at 700°C) had the highest CO₂ dynamic adsorption capacity of 2.10 mmol/g in a 7% CO₂/83% N₂/10% H₂O wet stream at 50°C and 130 kPa. AC with an adequate micropore volume and high amounts of pyridinic-like nitrogen species (pyridine and pyridine-N-oxide) and pyrrole-like nitrogen species is responsible for the superior CO₂ adsorption performance. These results suggest that nitric acid pre-oxidation followed by amination treatment at 700°C is a promising surface modification process for the production of carbon-based CO₂ adsorbents for post-combustion power plant flue gases with 5–10% saturated water vapor.
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